

# VOLTAMMETRIC STUDIES OF DIAMOND FILM ELECTRODES IN 0.5 M H<sub>2</sub>SO<sub>4</sub> WATER-ETHANOL SOLUTIONS

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## Abstract

Diamond films doped with B, N, Si or P are being extensively studied as electrode material because of their quasi-metallic conductivity, high chemical inertness and resistance to corrosion [1,2]. Among the many interesting and practical electrode reactions, undoubtedly the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) are two of the most important processes to be studied because of their importance in energy generation and storage and in the production of hydrogen peroxide, widely used in the paper and cellulose industry among others. Quite recently it was thought that diamond films were inert in aqueous solutions. However, it was shown [3] that when it was submitted to an anodic going potential excursion some interfacial processes occurred prior to the OER, which are still to be thoroughly studied.

This communication reports on the study of the E/I potentiodynamic behavior of boron doped (5000 ppm) diamond film electrodes in aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> and in water/ethanol mixtures. The experiments were performed at room temperature and all the potentials are referred to the Ag|AgCl|KCl(std.) reference electrode.

The typical cyclic voltammogram obtained for the diamond film electrode in aqueous 0.5 M H<sub>2</sub>SO<sub>4</sub> at 120 mV s<sup>-1</sup> showed that the HER and OER initiated at -0.2 V and 1.9 V, respectively. During the anodic potential scan only capacitive current was observed for approximately E < 1.1 V. For 1.1 V < E < 1.9 V, a small current increased slowly with E before the steep increase due to the OER. During the cathodic scan a small current was observed in the whole potential range. Experiments run with different anodic limit potentials, E<sub>λa</sub>, revealed that for E<sub>λa</sub> ≥ 1.8 V, the more anodic E<sub>λa</sub> bigger is the cathodic charge, showing that the cathodic charge is associated with interfacial species. When the cyclic voltammograms were obtained with varying initial potentials in the range -0.4 V ≤ E<sub>i</sub> ≤ +1.5 V, for a fixed anodic limit of E<sub>λa</sub> = 1.9 V, two different voltammetric behavior were observed. For E<sub>i</sub> > -0.2 V, the current related with the oxygen evolution (I<sub>O</sub>) at a fixed potential varied very little with E<sub>i</sub>. However, for E<sub>i</sub> ≤ -0.2 V, as E<sub>i</sub> decreased, I<sub>O</sub> increased significantly. This shows that the HER influences the kinetic of the OER. The electrode did not present any noticeable changes in its voltammetric behavior after anodic polarizations. However, after cathodic polarizations, a small anodic current peak was noted at c.a. 0.26 V that disappeared during the subsequent potential scan. Furthermore, the OER occurred at lower potentials and with higher currents. It was also seen that the E/I potentiodynamic behavior presented by the electrode before the cathodic perturbations was restored after an anodic perturbation.

When the solvent was replaced by water/ethanol mixtures, the voltammograms showed two anodic peaks at c.a. 0.4 V and 0.7 V which increased with increasing ethanol content and increasing potential sweep rate. The observed features are explained in terms of alcohol interaction with the electrode surface.

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